The Fusion Curve of Ammonia and Ethyl Alcohol

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Only within the last few years has any work been done on the fusion curves of ammonia and other substances. For many years the monohydrate of NH_3 was considered a compound, but not until Phase Law methods were followed has it and have similar compounds been obtained in the solid state. Work on the system $NH_3 + H_2O$ has been done by Rupert,[1] resulting in the formation of the compounds $NH_3.H_2O$ and $2\ NH_3.H_2O$. A little later the systems $(CH_3)_2O + NH_3$ and $CH_3\ OH + NH_3$ were investigated by Baume and Perrot.[2] These men succeeded in causing the formation of the compounds $(CH_3)_2\ O.NH_3$ and $CH_3\ OH.\ NH_3$. Since C_2H_5 OH and NH_3 are soluble in all proportions, it was expected that this system would give a curve somewhat similar to those mentioned above. In some respects it was found to be similar, in others quite different. The four curves will be shown together.

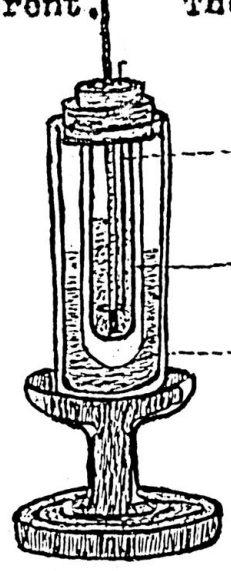


Fig. 1.

(1) Jr. Am.Chem. Soc. XXXI, 1909, p.866.
(2) Compt. Rend. 151. Sept. 5, 1910. p. 528.

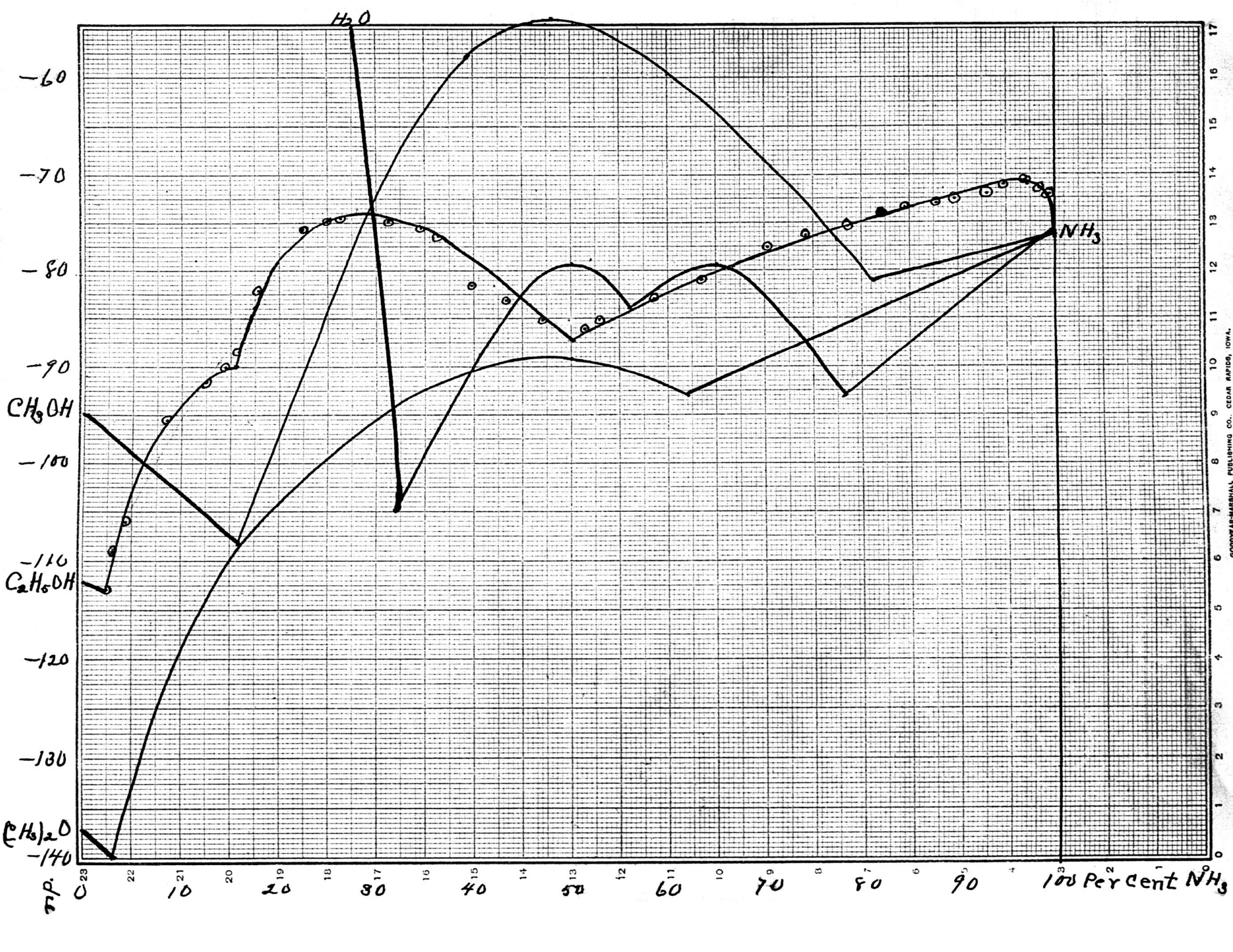
The apparatus used in determining the freezing point is given in Figure 1. It consisted of a (A) large test-tube, with thermometer and stirrer, enclosed within (B) a larger tube made of large glass tubing. The whole was then placed in (C) a vacuum jacketed cylinder filled with liquid air. Another jacketed cylinder was used to keep the temperature as nearly constant as possible while the crystals were beginning to form. A pentane thermometer, graduated in whole degrees and having a range of + 10 to -200° C. was used. The composition of the various solutions was determined by weighing a certain amount of NH_3 and calculating, approximately, the volume of C_6H_5OH in order to give the desired percentage. The C_6H_5OH + NH_3 was then weighed and the exact percentage of the solution determined. The weighing was done by introducing the miner test-tube, after a temperature of several degrees below the freezing point had been obtained, into a small jacketed cylinder and weighing the whole, in order to prevent any loss by evaporation. In transferring the test-tube from one cylinder to the other, some moisture was condensed on the surface, and of course would be a source of error, but not large

enough to make any appreciable difference in results. The pentane thermometer has a considerable temperature lag and as a result much trouble was experienced in getting the temperature when the crystals first began forming. This was partially remedied by cooling the solution until crystals formed and then by allowing the crystals to melt very slowly until only a few were left Results were obtained which checked within .5 of a degree. The slow warming was accomplished by introducing the two inner tubes into a cylinder ~~flask~~ with a little liquid air in the bottom. By having the warming take place so slowly, the source of error due to the temperature lag of the thermometer was almost entirely removed.

Another difficulty met was that of supercooling, especially when the composition was near the 100% alcohol. One solution was found to supercool over 50°, the solution becoming so thick that it could not be stirred at all. It was found that by supercooling the solution a few degrees and then allowing it to warm slowly, the crystals would form quite readily.

Measurements of percentage composition and freezing points have been made as follows:

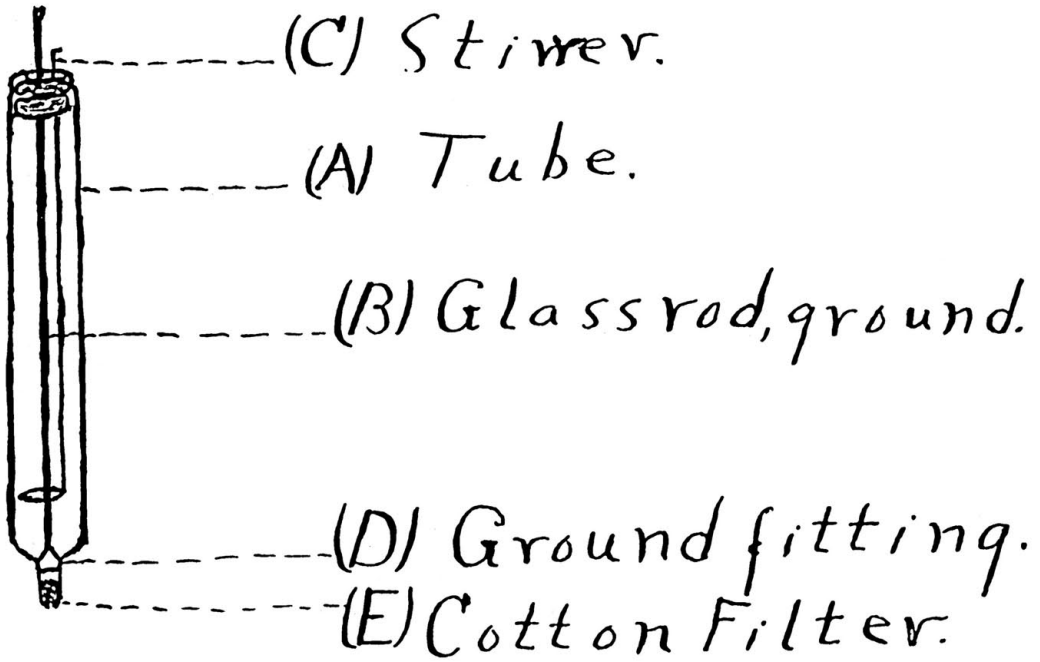
Per cent NH_3	Freezing Point Degrees C.	Per cent NH_3	Freezing Point Degrees C.
2.3	- 113	58.55	- 83.0
2.96	- 109	63.29	- 81.0
4.28	- 106	66.95	- 79.4
8.35	- 95.5	70.22	- 77.5
12.51	- 91.5	74.19	- 76.4
14.41	- 90.0	78.90	- 75.4
16.19	- 87.0	82.25	- 74.0
17.72	- 82.	85.14	- 73.5
22.50	- 75.5	87.77	- 73.0
24.78	- 74.8	89.89	- 72.5
26.33	- 74.5	93.00	- 72.0
31.28	- 74.8	94.73	- 71.0
34.57	- 75.5	96.91	- 70.5
36.33	- 76.5	97.02	- 71.2
39.80	- 81.5	98.52	- 71.5
43.36	- 83.0	99.25	- 71.5
47.27	- 85.0	99.37	- 71.7
51.38	- 86.0	99.62	- 73.5
52.90	- 85.0	100	- 76.5


H_2O
NH_3
CH_3OH
C_2H_5OH
$(CH_3)_2O$
-60
-70
-80
-90
-100
-110
-120
-130
-140
F.P.
0
10
20
30
40
50
60
70
80
90
100 Per Cent NH_3

From the curve (Figure 2), it will be seen that a well defined maximum freezing point occurs with a composition of about 28% NH_3 and a freezing point of -74.2°. The crystals coming down at this temperature and with the above composition are the compound $C_2H_5OH.NH_3$. The theoretical value for the per cent of ammonia in the compound is 27.87. From the freezing points of solution of about 15% NH_3, there seems to be a transition point at about -89.5 when the composition is about 15.5% NH_3. Because of the transition and maximum freezing points being so close together here, it has not been determined whether there really is a retrograde portion to the curve or whether at the maximum freezing point the compound is metastable when in contact with solution. The compound formed is $2(C_2H_5OH).NH_3$, the theoretical composition of which is 15.59% NH_3. Both compounds gave small colorless crystals which seemed quite similar, with the exception of the 2 $C_2H_5OH.NH_3$ being a little more needle-shaped.

It was expected that another eutectic would be formed near the 100% NH_3, but this was not found to be the case. Instead, when pure NH_3 was used and small quantities of C_2H_5OH introduced, the freezing

point rose rapidly to a maximum at about 97% NH_3 and then dropped down to a eutectic at about 50% NH_3. It is possible that a eutectic was formed so close to the freezing point of pure ammonia that it was not found, and because of that experiments were performed to see whether this maximum really represented another compound or whether it was a solid solution. The method used for this was to separate some of the crystals and analyze them to see how their composition compared with that of the solutions. Trouble was experienced in getting all of the mother liquor away, as the liquid was too viscous to be poured readily. A small tube



(A) (Figure 3) was drawn out at the bottom about one inch and the opening left small. The upper part of the drawn out end was ground and fitted with a ground glass rod (B) which could be removed from the top. In the lower part of the drawn out end was a small piece of cotton (C) used as a filter. After some of the crystals had been formed the ground glass rod and stirrer were removed and air that had been dried and cooled, was forced through the tube driving off the mother liquor quite completely. The crystals were analyzed by driving off the NH_3, collecting it in water, and titrating using $\frac{N}{10}$ HCl and methyl orgnge as indicator.

Measurements made are as follows:

Per cent NH_3 in solution	Per cent NH_3 in crystals
99.62	97.21
98.13	94.51
94.67	90.67
87.86	92.17
79.70	81.46
78.70	86.28
74.03	81.07

While there are several discrepancies in these results, they seem to indicate that a solid solution is formed rather than a compound. This part of the work will be further investigated, as will also the freezing points near the 100% of alcohol.

The curves for the systems $NH_3 + H_2O$, $NH_3 + (CH_3)_2O$ and $NH_3 + CH_3OH$ are given with the curve for the system $NH_3 + C_2H_5OH$ in order to make the comparison. By letting NH_3 be represented by R and C_2H_5OH, $(CH_3)_2O$, CH_3OH or H_2O by A, we have formed in each system the compound AR and in the systems $NH_3 + H_2O$ and $NH_3 + C_2H_5OH$, we have in addition the compounds A_2R. As was mentioned above, unlike the other systems, that of $C_2H_5OH + NH_3$ seems to show the formation of a solid solution near the 100% of NH_3.

The progress of the work has been due largely to the suggestionSand assistance of Dr. H. P. Cady to whom I wish to acknowledge my gratitude.